



The testing of batteries linked to supercapacitors with electrochemical impedance spectroscopy: A comparison between Li-ion and valve regulated lead acid batteries

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HIGHLIGHTS

- SoC testing of Li-ion or VRLA batteries with supercapacitors at 2 F:1 Ah ratio.
- Only slight improvement in the charge capacity acceptance for Li-ion systems was observed.
- Good improvement in the charge capacity acceptance for VRLA systems.
- EIS study confirmed the role of supercapacitor at various SoC.

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ABSTRACT

For electric vehicles, a supercapacitor can be coupled to the electrical system in order to increase and optimize the energy and power densities of the drive system during acceleration and regenerative braking. This study looked at the charge acceptance and maximum discharge ability of a valve regulated lead acid (VRLA) and a Li-ion battery connected in parallel to supercapacitors. The test procedure evaluated the advantage of using a supercapacitor at a 2 F:1 Ah ratio with the battery types at various states of charge (SoC). The results showed that about 7% of extra charge was achieved over a 5-s test time for a Li-ion hybrid system at 20% SoC, whereas at the 80% SoC the additional capacity was approximately 16%. While for the VRLA battery hybrid system, an additional charge of up to 20% was achieved when the battery was at 80% SoC, with little or no benefit at the 20% SoC. The advantage of the supercapacitor in parallel with a VRLA battery was noticeable on its discharge ability, where significant extra capacity was achieved for short periods of time for a battery at the 60% and 40% SoC when compared to the Li-ion hybrid system. The study also made use of Electrochemical Impedance Spectroscopy (EIS) with a suitable equivalent circuit model to explain, in particular, the internal resistance and capacitance differences observed between the different battery chemistries with and without a supercapacitor.

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1. Introduction

Li-ion batteries have comparatively higher energy densities by weight when compared to other battery chemistries and have shown great potential for their use in EV and HEV applications [1]. However, the battery is limited in its ability to accept large amounts of charge over a short period of time [2]. In order to optimize the battery management system (BMS) within a vehicle, the batteries are usually oversized for a particular application in order to accommodate the excessive charging or discharging. This increases the overall weight and costs of the vehicle [3]. Supercapacitors can be added to a battery in an EV application in order to relieve the

battery during the severe load demands such as regenerative braking (charging) or vehicle acceleration (discharging) [3]. The energy supply system will then be able to deliver the average power load without the need for an oversized battery configuration which, in some cases, has demonstrated a saving of up to 60% in weight through a well-designed battery and supercapacitor configuration [2,4]. The study by M. Fernández et al. [5] considered a 6 V/24 Ah Pb-acid battery coupled with a 52 F supercapacitor. The study considered the high rate charging and discharging ability of a Pb-acid battery at different States of Charge (SoC) with and without a supercapacitor. The study showed the important role of a supercapacitor when connected in parallel with a battery to accommodate a higher charge acceptance, but also in-turn, to provide additional energy when a higher discharge was required. This was particularly important for systems that make use of Pb-acid batteries, where poorer charge acceptance was expected at lower

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SoC, due to the nature of its chemistry, and also that the life of the battery is significantly shortened if it is kept in a partial state of charge for considerable lengths of time [6]. The high rate charging or discharging required is usually only for a few seconds, where a supercapacitor would be well suited to accommodate such demands. A similar study was done by D. Shin et al. [7] that showed that Li-ion batteries can be connected to supercapacitors via a new hybrid energy storage system using a constant-current regulator. The system allowed for the energy density to be regulated thereby optimizing its efficiency and limiting the high rate capacity degradation of the Li-ion cells that was often associated with high load currents.

Supercapacitors have superior cycle efficiency but are comparatively costly when compared to battery storage systems where their volumetric energy density per unit of stored energy is considerably less [7]. However, one can consider a hybrid system, where the advantages of the high power capabilities of supercapacitors would store the surplus energy that can be combined with the suitability of a high volumetric energy density battery such as a Li-ion battery that can effectively work in variable high power applications such as EV, Fuel cell vehicles and HEV. The BMS would regulate the battery and supercapacitor to maximise the deliverable energy density that would also take into account any required terminal voltage variation associated with the supercapacitor and prevent the battery, especially for Li-ion batteries systems, to under discharge or overcharge.

The following study compared the combination of supercapacitors with two types of battery energy systems (Li-ion and VRLA) that were subjected to different charge and discharge conditions at different SoC. The maximum current that could be attained during the charge or discharge from a system would be set within the voltage limits established by the battery manufacturer. The upper and lower voltage limits for the Li-ion type battery are strictly limited by the chemistry in the cell. Over-charging or under-discharging would result in chemical phase changes within the active electrode material thereby causing irreversible damage. On the other hand, Pb-acid batteries allow for short periods of over-charging, but are more susceptible to active material damage during over-discharging or capacity cycling at a partial state of charge. In addition, Electrochemical Impedance Spectroscopy (EIS) measurements were also done on the systems at the various SoC to possibly describe differences using suitable equivalent circuit models.

2. Experimental

A capacity testing procedure was carried out in order to compare the charge acceptance and discharge ability of a battery alone against a system consisting of a battery and a supercapacitor (hybrid system). A ratio of 2:1 (supercapacitor (F): battery (Ah)) was used in the study that was similar to the one described by M. Fernández et al. [5]. 2.4 Ah Li-ion cylindrical cells and 5.2 Ah VRLA cells were used in the study. For comparison purposes, the Li-ion cells were connected in series to achieve a similar battery capacity to that of the VRLA battery, and two VRLA cells were connected in parallel to achieve similar battery voltages to that of the Li-ion battery. Two 10 F supercapacitors were connected in series to each other in order to accommodate the higher battery voltages and then in parallel to the two battery systems respectively.

Each battery system (with and without a supercapacitor) were subjected to a program that discharged it at the C1 rate to a particular State of Charge (SoC). This was followed by a 5-s high rate charge with an upper battery voltage of 4.2 V or a 10-s high rate discharge with a lower voltage limit of 3.0 V for the Li-ion battery.

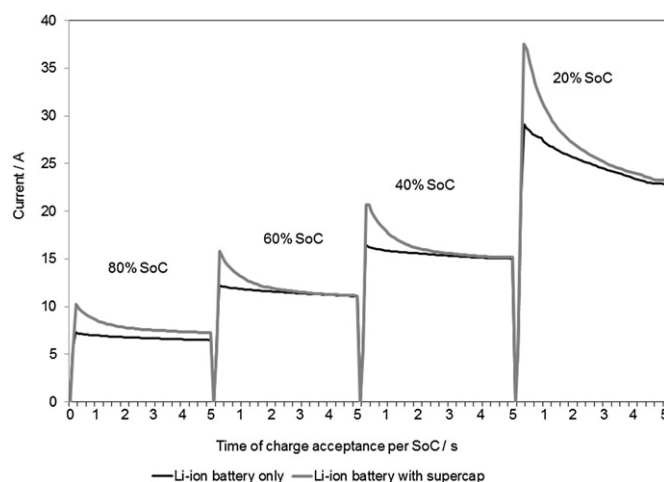


Fig. 1. The 5 s charge acceptance comparison between the Li-ion batteries with and without the supercapacitors at different SoC.

The VRLA battery was limited to an upper voltage limit of 5.3 V during the charge and 3.3 V during discharge. The batteries were then fully recharged, followed by the discharge to another SoC after which the 5-s high rate charge and 10-s high rate discharge step were then repeated. The capacity testing program sequences were done on a Bitrode LCV50 multi-channel tester. All tests were done in triplicate to show their repeatability.

Electrochemical Impedance Spectroscopy (EIS) was carried out on a Gamry Reference 3000 set in Galvanostatic mode with a scan frequency range between 0.025 and 60 000 Hz for all batteries assembled with or without the supercapacitors. EIS spectra were taken at the four SoCs for each battery type with and without supercapacitor. The spectra were then analysed using an equivalent circuit model that was described by D. Andre et al. [8,9].

3. Results and discussion

3.1. SoC variation of 4.8 Ah Li-ion and 5.2 Ah VRLA batteries with 10 F supercapacitors

The comparative studies of the charge acceptance at different SoC within the upper voltage limits of 4.2 V for the Li-ion batteries with and without the supercapacitors are shown in Fig. 1. The respective differences between initial maximum acceptance current of the battery with the supercapacitor and that of the battery alone are summarized in Table 1. The total capacities (mAh) achieved by the two systems over the 5-s charge period are also shown.

The results showed that the analysis was repeatable over three sets of experiments where there was an increase in the maximum peak current that the system with the supercapacitor could accept

Table 1

The initial increase in current (A) at each SoC of the Li-ion battery with and without capacitor and the total comparative capacity (mAh) increase at each SoC over the 5-s high rate charge below the upper voltage limit of 4.2 V.

SoC	Increase in peak charge current (A)	Capacity over 5-s step (mAh)		Total comparative capacity increase (mAh)
		Li-ion battery	Hybrid system	
80%	2.96 ± 0.01	9.2 ± 0.2	10.7 ± 0.2	1.5
60%	3.52 ± 0.02	15.8 ± 0.5	16.6 ± 0.3	0.8
40%	4.42 ± 0.04	22.5 ± 0.8	23.7 ± 0.5	1.2
20%	8.37 ± 0.03	35.7 ± 0.5	38.2 ± 0.3	2.5

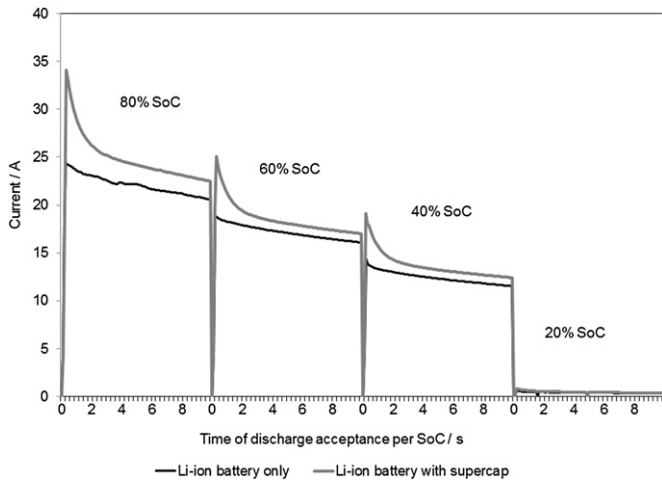


Fig. 2. The 10 s discharge comparison between the Li-ion batteries with and without the supercapacitors at different SoC.

at the various SoC of the battery. Notably, as the SoC decreased, the maximum peak charge current of the hybrid system would increase when compared to the battery by itself, where the charge current differences would decrease relatively quickly within the 5-s test. At the 20% SoC, the hybrid system showed an increase of accepting 7% more charge capacitance when compared to that of the battery alone. Notably, the additional charge acceptance at the higher 80% SoC was about 16%.

The comparative studies of the high rate discharge ability with a lower voltage limit of 3.0 V for the Li-ion batteries with and without the supercapacitors are shown in Fig. 2. The differences between the initial maximum deliverable current of the battery with the supercapacitor and that of the battery alone are summarized in Table 2. The total discharge capacities achieved by the two systems over the 10 s discharge period are also shown.

The results showed that as the SoC decreased, the amount of additional charge that could be delivered also decreased. The comparison between the capacities (mAh) of the battery alone against the hybrid system showed that up to a 40% SoC, the battery with the supercapacitor was able to deliver slightly more current at the beginning of the discharge step with an additional 9% capacity over the 10-s period when compared to the battery without capacitor. However, the battery that was only at 20% SoC achieved very little additional discharge capacity with a supercapacitor when compared to the battery alone.

In a paper by C.E. Holland et al. [10], a 50 F supercapacitor was added in parallel to a 1.2 Ah Li-ion battery for pulse duty applications. When the Li-ion cell was paired with the supercapacitor, only a slight improvement was observed in terms of achievable power. This meant that the supercapacitor assumed a higher percentage of the load current but did not necessarily improve the overall

Table 2

The initial increase in current (A) at each SoC of the Li-ion battery with and without capacitor and the total comparative capacity (mAh) increase at each SoC over the 10-s high rate discharge above the lower voltage limit of 3.0 V.

SoC	Increase in peak discharge current (A)	Capacity over 10-s step (mAh)		Total comparative capacity increase (mAh)
		Li-ion battery	Hybrid system	
80%	9.66 ± 0.02	60.1 ± 0.9	67.6 ± 0.9	7.5
60%	6.34 ± 0.01	46.8 ± 0.8	50.6 ± 0.4	3.8
40%	4.80 ± 0.01	33.9 ± 0.8	37.3 ± 0.3	3.4
20%	0.28 ± 0.01	1.11 ± 0.04	1.3 ± 0.1	0.2

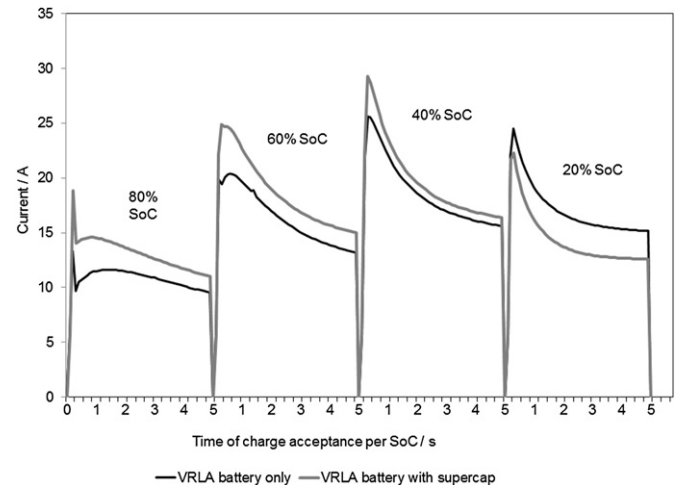


Fig. 3. Comparison between the Pb-acid battery and the system of Pb-acid battery and supercapacitors using the high rate charge current.

capacity. In order to improve the power available from the system, the current would have to be better controlled by sharing the current between the components within the system. In addition, there were weight problems in the system when large capacitors (50 F) were used, giving no real benefit to the system when its comparative weight contribution was also considered. The present study showed that a comparatively smaller supercapacitor can still give a slight improvement to the charge acceptance of the hybrid system. However, care needs to be taken not to allow the battery to discharge below 20% SoC. Below this SoC of the battery, there was very little discharge benefit of the additional supercapacitor within the voltage limits. However, at this SoC significant additional recharge capacity over a short period of time can be achieved within the upper voltage limit.

The comparative studies between the high rate charge acceptance of the VRLA battery below the upper voltage limit of 5.3 V with and without supercapacitor are shown in Fig. 3. The respective differences between initial maximum acceptance current of the battery with the supercapacitor and that of the battery alone are summarized in Table 3. The total capacities achieved by the two systems over the 5 s charge period are also shown.

The results showed a comparative decrease in the acceptable peak charge current as the SoC of the battery decreased. The charge acceptance at 80% SoC showed the typical sharp peak that was followed by a sudden decrease in current. This effect is known as the “coup de fouet” effect and is common to Pb-acid batteries that are subjected to high discharge rates [11]. In this study, this effect was observed during the high rate charge sequence. During the initial stages of charge, the electrode surface can accept a large proportion of the current, but with time the electrodes get quickly saturated and the charge acceptance then becomes

Table 3

The initial increase in current (A) at each SoC of the VRLA battery with and without capacitor and the total comparative capacity increase at each SoC over the 5-s high rate charge.

SoC	Increase in peak charge current (A)	Capacity over 5-s step (mAh)		Total comparative capacity increase (mAh)
		VRLA battery	Hybrid system	
80%	5.54 ± 0.03	14.6 ± 0.4	17.6 ± 0.8	3.0
60%	4.49 ± 0.03	21.9 ± 0.4	25.0 ± 0.3	3.1
40%	3.69 ± 0.01	25.1 ± 0.3	26.6 ± 0.9	1.5
20%	-2.21 ± 0.01	23.0 ± 0.6	19.4 ± 0.1	-3.6

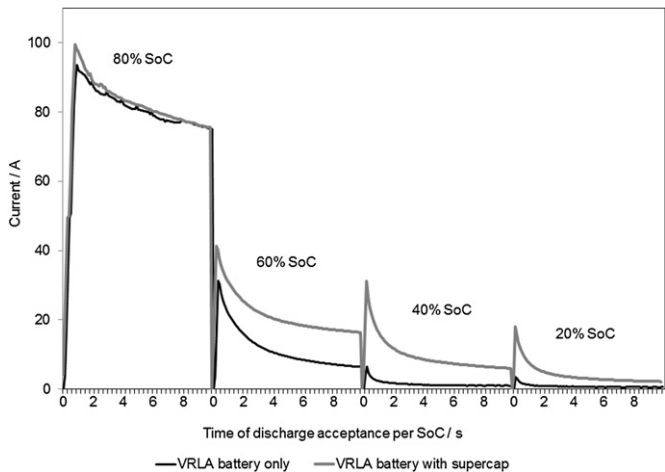


Fig. 4. The 10 s discharge comparison between the VRLA batteries with and without the supercapacitors at different SoC.

diffusion-limited to the bulk of the porous material and electrolyte. This effect is partially reduced with the addition of a supercapacitor and not obvious for the batteries that were at 60% and 40% SoC. The results showed that an improvement of up to 20% comparative capacity at the 80% SoC and 14% capacity at the 60% SoC was achieved over the 5 s of charging (Table 3). Furthermore, the results in Fig. 3 showed that there was still a difference in the comparative charge currents of the battery only and the hybrid after 5 s of charging at the 80% and 60% SoC, indicating that there was still additional charge difference available. Noticeably, the advantage in terms of additional charge acceptance of a supercapacitor at the lower SoC decreased, where, at the 20% SoC, the battery without the supercapacitor was able to accept more peak current and charge capacitance than the hybrid system over the 5-s charge step. This result was unusual and significantly different to the study with the Li-ion battery. The experiments were repeated and the same phenomena were observed.

This unusual phenomenon was repeatedly observed implying that the resistance of the combined battery and supercapacitor was comparatively higher than that of the battery at the 20% SoC. At different SoC, the internal resistance of a VRLA Pb-acid battery will have an effect on the charge acceptance. These results were different to the results observed by Fernandez et al. [5], where the difference might be due to the difference in the test procedure used. The test sequence used in this study allowed the battery and/or supercapacitor to fully recharge before discharging at the C_1 rate to the 20% SoC. The test procedure and results published by Fernandez et al. [5] seemed to be sequential where after each analysis at a SoC, the battery was further discharged to the next SoC.

The comparison between the VRLA battery with and without supercapacitors that were discharged at different SoC are shown in

Table 4
The initial increase in current (A) at each SoC of the VRLA battery with and without capacitor and the total comparative capacity increase at each SoC over the 10-s high rate discharge.

SoC	Increase in peak discharge current (A)	Capacity over 10-s step (mAh)		Total comparative capacity increase (mAh)
		Battery	Hybrid system	
80%	6.20 ± 0.02	226.3 ± 0.2	230.5 ± 0.1	4.2
60%	10.00 ± 0.03	31.5 ± 0.9	59.0 ± 0.9	27.5
40%	24.69 ± 0.02	4.1 ± 0.1	26.5 ± 0.9	22.4
20%	14.40 ± 0.01	2.29 ± 0.04	11.4 ± 0.6	9.1

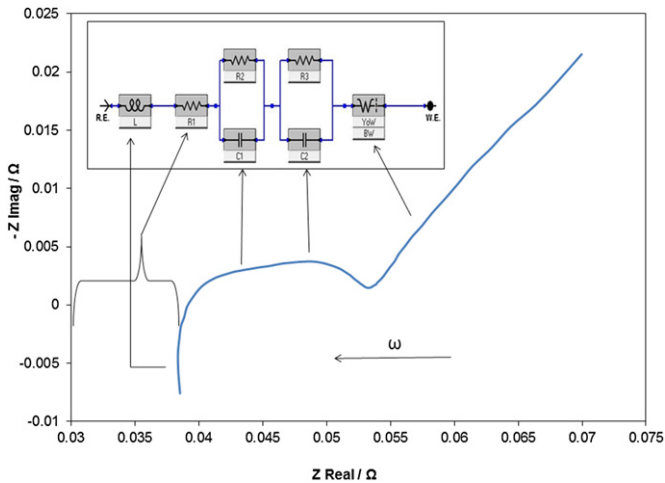


Fig. 5. An example of an impedance spectrum and EIS model used to analyse a fully charged Li-ion battery.

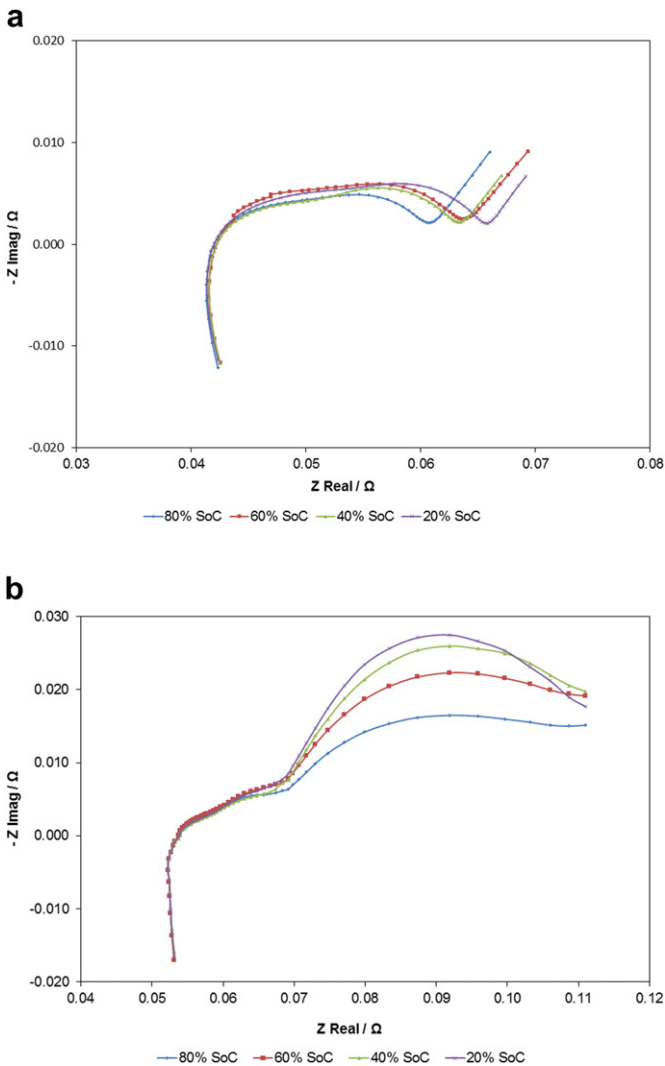


Fig. 6. The EIS spectra of the (a) Li-ion battery only and (b) the hybrid system at different SoC.

Table 5

The EIS equivalent circuit model parameters for the Li-ion battery with and without supercapacitor.

	R2 (mΩ)		R3 (mΩ)		C1 (F)		C2 (F)		W (S sec ^{1/2})	
	Battery	Hybrid	Battery	Hybrid	Battery	Hybrid	Battery	Hybrid	Battery	Hybrid
80%	8.742	19.455	6.725	8.346	1.508	1.481	0.090	0.963	227.7	119.8
60%	11.269	28.768	7.519	9.420	1.284	1.403	0.097	1.167	241.2	107.1
40%	9.856	34.412	7.911	9.822	2.107	1.360	0.095	1.073	292.5	113.7
20%	8.125	36.764	9.307	10.160	1.663	2.333	0.106	1.532	301.7	123.7

Fig. 4. The difference between initial maximum delivered current and the total capacity over the 10 s discharge are summarized in Table 4. The results showed that at the 60% and 40% SoC, a significant improvement in the discharge capacity of the hybrid battery over the 10 s test could be achieved when compared to the discharge ability of the battery alone. The added benefit of a supercapacitor at the 80% was not as obvious, where a comparatively high discharge current can be achieved over the 10-s test. However, the advantage of the supercapacitor was noted at the 60% and 40% SoC and decreased at the 20% SoC, but still showed a benefit in terms of achieving a larger initial peak current and significantly more capacity when compared to the battery alone. This could be due to the increase in internal resistance of the battery and supercapacitors that caused the system to quickly reach the lower voltage limit of 3.3 V. This could be improved slightly by decreasing the lower discharge voltage limit, but manufacturers recommend that the lower discharge voltage be kept within acceptable limits to reduce the effect of irreversible capacity loss due to over-sulphating of the electrodes. These results show that the VRLA type battery system can be comfortably capacity cycled above the 40% SoC in high current applications where a supercapacitor in parallel could contribute to its power management.

3.2. Electrochemical impedance spectroscopy of Li-ion and VRLA batteries with and without supercapacitors

In this study for the purpose of comparing the EIS behaviour of the two battery types with and without a supercapacitor, the spectra can be described by a simplified two electrode Randel's equivalent circuit model that is commonly used to describe the electrochemical battery [8,9]. The model relies on a set of parameters that describe the different regions of a typical EIS Nyquist plot of the imaginary impedance versus the real impedance spectra (Fig. 5). For each battery type with and without supercapacitor, the changes in these parameters were studied at each SoC.

The equivalent circuit used to describe the spectra is made up of various regions. The inductance (L) of the battery would occur at high frequencies and is due to the inductive reactance that results from the metallic components of the cell and sampling leads. "R1" would be the sum of Ohmic resistances of the current collectors, active material, electrolyte and the separator and occurs where the graph intersects the real impedance axis (x -axis). The regions of "R2" and "C1" would describe the first semi-circle of the spectra and is usually associated with the Solid Electrolyte Interface (SEI) layer in a Li-ion cell that is formed on the anode during cycling and the shape of the semi-circle will change as the cell ages. The region labelled "R3" and "C2" forms part of the second semi-circle which represents respectively the charge transfer resistance and double layer capacity of the electrodes and will also change as the cell ages. The regions of "YoW" and "BW" can be described by the Warburg element (Z_w) related to the diffusion processes in the active material of the electrodes at very low frequencies. A Warburg element in an equivalent circuit model would in simple terms describe the distance the diffusing reactants travel within the cell.

At high frequencies, the Warburg element is relatively small as the diffusing reactants don't need to travel very far; however at lower frequencies, the Warburg element is larger as the diffusing reactants need to move further between the oscillating frequencies. In the batteries studied, a bonded Warburg element was used that took the nature of the separator into consideration.

The EIS Nyquist plots of the Li-ion battery with and without supercapacitors at the different SoC are shown in Fig. 6 and the calculated results of fitting the equivalent model to the various spectra are summarized in Table 5.

There were slight differences in the electrode resistance components within the first semi-circle which corresponded to the resistance associated with the SEI (R2) that forms on the anode

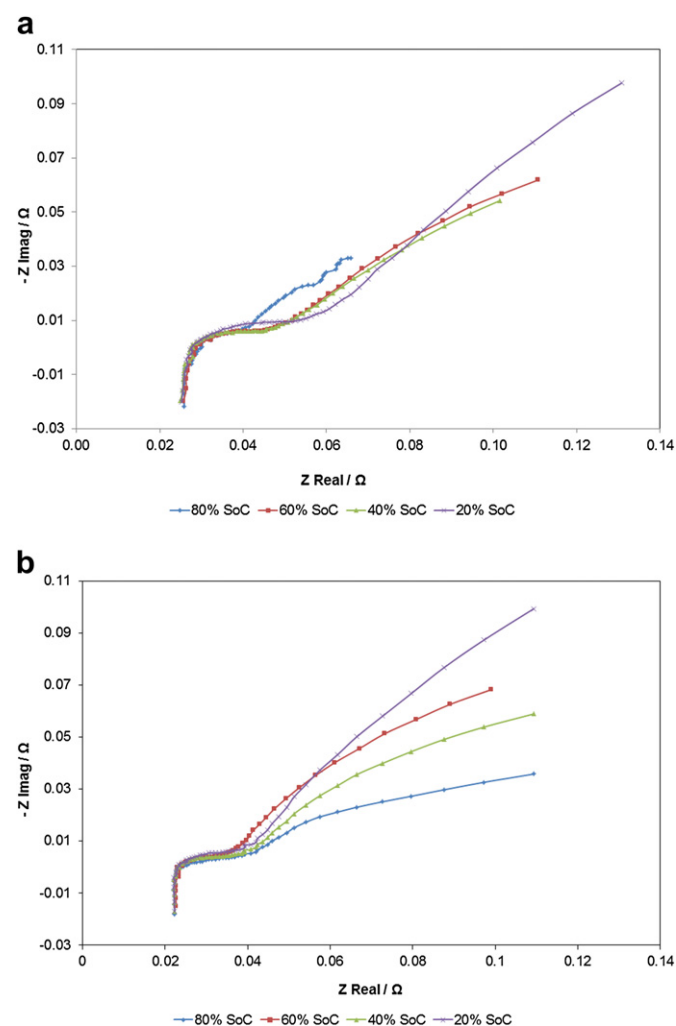


Fig. 7. (a) The EIS spectra of the VRLA battery at different SoC. (b) The EIS spectra of the VRLA hybrid system at different SoC.

Table 6

The EIS equivalent circuit model parameters for the VRLA battery with and without supercapacitor.

	R2 (mΩ)		R3 (mΩ)		C1 (F)		C2 (F)		W (S sec ^{1/2})	
	Battery	Hybrid	Battery	Hybrid	Battery	Hybrid	Battery	Hybrid	Battery	Hybrid
80%	7.178	2.886	4.083	1.623	2.338	3.849	0.291	0.622	59.69	45.54
60%	8.399	3.553	5.291	1.934	0.580	0.599	0.063	0.178	33.00	28.97
40%	9.111	4.208	5.467	2.413	0.694	0.773	0.084	0.174	34.00	31.55
20%	12.234	5.058	5.536	2.148	0.575	0.696	0.089	0.162	28.00	23.77

surface. This implied that the partial resistance within the capacitor contributed to this parameter due to its low discharge state. There were also differences within the second semi-circle which corresponded to the resistance associated and charge transfer resistance (R3) at the electrodes. The capacitance (C1) associated with the anode showed only small differences between the cells with and without capacitor where a notable increase in the value was observed at the 20% SoC of the battery. There was, however, a significant difference between the observed values for the double layer capacity (C2) when the supercapacitor was included in parallel with the battery. The capacitance associated with the double layer capacity and charge transfer resistance (R3) of the hybrid system showed greater capacitance than the Li-ion cell alone. The capacitance considered at the SEI layer increased from 20% SoC to 80% SoC which was in agreement with the trend in increase in the cells high discharge rate tests. However, the capacity parameter that considered the capacitance at the electrodes showed a slight decrease from 20% to 80% SoC. A relative similar capacitance at C2 was observed for the Li-ion cell alone, while the same capacitance for the hybrid system showed an increase with decreasing SoC.

A notable change was also observed in the Warburg parameter (W) where the 45° angle at the lower frequencies of the graphs would correspond to a semi-infinite diffusion. Deviation from this slope would be due to the effect of porous structure and particle size distribution on the diffusion-related impedance in the active particles [12]. The results showed that the additional semi-circle increased and became more distinct as the SoC of the hybrid battery decreased, implying that the capacitor contribution increased (Fig. 6b).

A measure of the time taken for the reactant to diffuse across the Nernst Diffusion layer is characterized by the Warburg parameter (W) in the equivalent circuit model. The Nernst Diffusion layer is a virtual layer, within which the gradient of the ion concentration is constant and equal to the true gradient at the electrode–electrolyte interface. The results showed that the Warburg impedance parameter determined for the Li-ion battery alone were significantly higher in values than for the hybrid system. Capacitors have an imaginary impedance component, and the current through a capacitor is phase shifted through -90° with respect to the voltage. A capacitor in series to the cell would dominate the imaginary impedance component of the circuit [13]. This would imply that the overall impedance for the system would be lower and a smaller Warburg constant would be seen. The slightly higher Warburg values at the lower SoC of the cell would only indicate that longer time periods for the reactants to diffuse through the Nernst Diffusion layer would be required.

During the discharge of the battery, the Li-ions are moved from the anode to the cathode. For the system that consists of the battery alone, as the SEI layer influenced the movement of the ions, the resistance (R2) would be slightly larger at 80% SoC and become smaller as the SoC decreased. However the resistance associated with the SEI layer for the hybrid system was comparatively higher at 20% SoC, and decreased as the SoC increased, with a notable

increase in the SEI capacitance. Comparatively, the capacitance associated with the electrodes decreased as the SoC of the system increased. Hence, this implies that the charge was predominantly located at the SEI surface. This supports the observations that during the high rate discharge testing higher charge delivery was seen for the cells with capacitor at 80% SoC.

The EIS spectra of both the VRLA battery with and without supercapacitor are shown in Fig. 7. The VRLA battery does not have the same SEI layer chemistry that is formed on the anode as was observed for the Li-ion battery. Instead, the anode's surface changes would be associated with the formation of a non-conducting sulphate layer. This would be the formation of lead sulphate which will have an effect on both the resistance and capacitance of the electrode. As the battery is discharged, the active material changes to the lead sulphate where the size of the available active surface will decrease and its resistance would increase. With time, as the battery ages or is capacity cycled, the lead sulphate deposit usually increases in size thereby reducing the available active surface area and an increase in resistance would be measured [6].

The changes in the EIS equivalent circuit model parameters are summarized in Table 6, where the resistance contribution (R2) associated with the surface layer at the anode increased as the SoC for the battery alone decreased. Noticeably, the capacitor in parallel to the battery would reduce this value. The surface resistance on the anode at low SoC would increase due to the formation of a predominantly insulating layer of PbSO₄.

The associated capacitor (C1) value would comparatively show little difference between the battery with and without supercapacitor. However, the capacitor C2 showed a comparative increase when the battery was in parallel with a supercapacitor. The cell with the supercapacitor had a significantly higher capacitance value at the 80% SoC than the cell without the capacitor which can be associated with surface charge that was present on the surface of the electrodes at the SoC. The Warburg parameters of the circuit were similar in magnitude for the different SoC for the battery with or without supercapacitor.

4. Conclusion

The study showed that supercapacitors can be used in parallel with energy storage systems such as Li-ion and VRLA type batteries at the 2 F:1 Ah ratio giving different characteristics and capacity performance at various SoC. The electrochemical behaviour and possible advantages of such hybrid systems are different for different cell chemistries and their management in applications should be factored into the BMS when dealing with currents that result from regenerative braking and their possible use in auxiliary systems, or even for smoothing power delivery. The study showed that the charge acceptance ability for a supercapacitor system with a Li-ion or VRLA type battery behave significantly different from each other within their respective charge voltage limits. The Li-ion hybrid system readily accepted charge as the various SoC, with a fast decrease in the charge current within the 5-s charge test to be similar to the battery only charging profile. This resulted in that the added capacity achieved with a supercapacitor was only in the

order of about 7% at the 20% SoC and about 16% at the 80% SoC respectively. With regards to the VRLA battery system, there was a notable increase of about 20% and 14% in charge acceptance at the 80% and 60% SoC of the battery with a supercapacitor. This however decreased significantly at the 40% and 20% SoC. With regards to the discharge tests at the various SoC of the two hybrid systems, the study showed that there was a significant advantage of using the supercapacitor with a VRLA battery at the 40% and 60% SoC. The added benefit of a supercapacitor with a Li-ion battery during discharge was not as apparent where a notable difference in the high current rates was significantly lower for a comparatively similar Ah rated system when compared to the VRLA system.

The VRLA battery could achieve comparatively higher discharge currents at the higher SoC when compared to the Li-ion battery. However, at the slightly lower SoC (60% and 40%), the achievable discharge currents were comparatively similar for the two battery type systems without the supercapacitors. These differences would primarily be associated with the differences in electrolyte chemistry and electrode configuration, where the VRLA aqueous system should be able to deliver higher currents and have a significantly larger porous electrode surface to accommodate for comparatively higher currents. However, working the VRLA battery at a partial state of charge would quickly result in a poorer current delivery where the added benefit of a supercapacitor was shown. In this study, the weights of the respective battery systems were not considered but would play a significant role when larger power units are required in applications such as HEV or EV. The Li-ion battery system would obviously have an advantage in terms of its volume and weight considering all other factors being equal.

The study also showed that the impedance behaviour of the two energy storage systems with and without supercapacitors were different. The resistance values for the VRLA systems were higher than the values of the Li-ion hybrid systems. However the capacitance was higher for the VRLA Pb-acid hybrid system than for the

Li-ion hybrid system with higher Warburg impedance values for the Li-ion hybrid system, which could explain its better charge acceptance; however, the discharge delivery of the VRLA hybrid system was better than the Li-ion hybrid system respectively.

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